

# PATENT SPECIFICATION

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DRAWINGS ATTACHED

1260 733

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 (72) Inventors MICHAEL THOMAS WESTAWAY and ALAN GOLDUP



## (54) MEMBRANE SEPARATION PROCESS

(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, E.C.2., a company incorporated in accordance with the Laws of England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to methods of separating organometallic compounds from solutions in non aqueous solvents.

It is frequently desirable to separate organometallic compounds from solution in organic liquids. A particular example of this is when such materials are used as catalysts in homogeneous catalysis. In some cases the reaction product containing catalyst is thermally unstable so hot separation by methods such as distillation may be inapplicable. Furthermore these materials are frequently very expensive and recovery by a method that does not result in degradation is particularly desirable.

Our copending application No. 12173/68 (Serial No. 1 243 507) discloses a process for the separation of a transition metal complex from solution in an organic component which comprises bringing the solution into contact with one side of a cellulosic membrane at an applied pressure greater than the pressure on the opposite side of the membrane, the pressure differential being greater than the osmotic pressure of the system.

Our copending application No. 51232/68 (Serial No. 1 243 508) discloses a similar process in which the membrane is a silicone rubber membrane.

It has now been found that separation can be achieved by using a membrane made from a polyolefin.

Thus, according to the present invention there is provided a process for the separation of an organometallic compound from a solution of the compound in an organic component which comprises bringing the solution into contact with one side of a polyolefin

membrane at an applied pressure greater than the pressure on the opposite side of the membrane, the pressure differential being greater than the osmotic pressure of the system and the molecular size and shape of the organometallic compound in relation to those of the organic component being such that under the applied pressure the permeate has a reduced content of the organometallic compound.

The invention further provides a process involving homogeneous catalysis which comprises reacting one or more organic components, in the presence of one or more organometallic compounds so as to produce a solution of the organometallic compound, the reaction being carried out in a reaction system having an outlet across which is disposed a polyolefin membrane, and separating the organometallic compound from the organic components as herein described.

The membrane can be external to the reaction system, for example in cases where the conditions of separation, for example temperature and/or pressure, differ from those of reaction. One or more separation steps other than membrane separation can exist between the reaction system and a membrane separation step external to it.

By the term organometallic compound we mean a compound containing a metal and an organic moiety. The term is not limited to compounds containing a metal to carbon bond.

Preferably, in a catalytic process the products and any unreacted components are separated from each other after having permeated the membrane and the unreacted components may then be recycled if desired. The metal can be a transition metal of Group VIII, VIIA or VA of the periodic table e.g. nickel or a non transition metal e.g. aluminium. Typical organometallic compounds are hydroformylation catalysts such as Rh (Bu<sub>3</sub>P) CO acac the Ziegler catalysts such as aluminium alkyls, alkoxides or alkylalkoxides.

"Organic components" referred to hereinbefore means compounds containing, carbon combined with one or more other elements,

for example, hydrogen, oxygen, nitrogen, sulphur and phosphorus, for example, alcohols, aldehydes, ketones, organic acids, phosphines and amines.

5 The process of the present invention may be operated at applied pressures up to at least 2500 psig. Preferably the applied pressure is in the range 100 to 2000 psig. Suitable operating temperatures are those below which dis-

10 solution of the membrane occurs and are generally in the range 0 to 100°C. Preferred temperatures are from 15°C. to 80°C. more especially below 60°C.

Suitable concentrations of the metal complex or compound are from above 0 up to

15 50,000 parts per million by weight.

Polyolefins which can be used in the preparation of the membranes are polyethylene, polypropylene, poly - 4 - methylpentene - 1 and polystyrene or a blend thereof. The polyethylene can be either of the forms of polyethylene known in the art as "high density" and "low density" polyethylene. Also suitable for the preparation of the membrane are polymer blends and copolymers of olefins for example a blend of polymers of propylene and 4 - methylpentene - 1. A suitable form of polyethylene which can be used, is "Rigidex" (Registered Trade Mark) high density Type 30 50 manufactured by BP Chemicals (U.K.) Limited. Rigidex Type 50 has a melt index of 5.0 g/10 min, in accordance with BS 2782 method 105C, a density of 0.96 g/ml in accordance with BS 2782 Method 509A and a softening point of 128°C. for a 60° deflection in accordance with BS 2782 Method 102C. A suitable polypropylene is manufactured by I.C.I. Limited and designated GW 40 522M and has a melt index in granules of 3.0 in accordance with BS 2782 Method 105C and a softening temperature of 148°C. in accordance with BS 2782 Method 102D. The polyolefin membrane can be a copolymer of monomers selected from ethylene, propylene and 4 - methylpentene - 1. The membranes can be prepared from solution in an organic solvent e.g. xylene by casting onto a glass plate and allowing the solvent to evaporate. The membrane can be removed from the plate by immersing in cold water. The membrane can then be dried and is ready for use.

50 It has been found that an annealing treatment of the membranes before use by immersing in an organic liquid at a temperature just below the dissolution temperature can increase the permeation rate.

Suitable organic solvents are xylenes, hexadecane and toluene. Preferably toluene is used.

55 Preferred temperatures are from 80 to 100°C. and suitable periods for immersion are from 1 to 20 hours.

The thickness of the membrane should be within the range 0.05 to 100 microns. The preferred thickness is 0.1 to 5 microns. The thickness of the membrane in the casting pro-

cess can be controlled by varying the concentration of the polyolefin solution and the rate of removal of the slide from the solution.

The membrane can be used either supported in a typical plate form or unsupported in the form of a hollow fibre. 70

The processes of the present invention are most suitably used when the concentration of metal organic compound is low and/or there is a large molecular size and weight difference between the metal compound and the organic components to be separated. In the case of a catalytic reaction most suitably there is as large a difference in molecular size and weight as possible between the metal compound and the reaction products. 80

The processes of the present invention can be employed in systems containing hydrocarbon components e.g. alkenes possibly in the presence of other hydrocarbon types having up to 20 carbon atoms per molecule and preferably 5 or less carbon atoms per molecule, in which hydrogen and/or carbon monoxide or carbon dioxide may be present and in which the metal organic compound contains one or more of metals of Group VIII of the Periodic Table according to Mendeleef and at least one biphyllic ligand and a bidentate ligand co-ordinating through at least one oxygen atom. Thus, for example, a suitable system in which processes of the invention can be used in that in which a lower olefin is hydroformylated in the presence of carbon monoxide and hydrogen and a rhodium complex in which the biphyllic moiety is tri *n*-butyl phosphine and the bidentate moiety is acetyl-acetonate i.e.  $\text{Rh}(\text{Bu}_3\text{P})\text{CO}(\text{acac})$ . The products from this reaction are alcohols and/or aldehydes, depending on the catalyst concentration, and the reaction is further discussed in our copending U.K. Patent Application No. 55295/67 (Serial No. 1 243 189). Another suitable system is that in which a lower olefin is dimerised in the presence of a nickel acetylacetonate complex promoted by aluminium diethylethoxide. 100

The membranes can also be used to separate nickel and vanadium porphyrins for example the etio porphyrins from hydrocarbon solvents such as toluene. 115

The membrane used can but need not necessarily be in the form of a disc. It should be in a form suitable to withstand the operating conditions to which it is subjected, particularly elevated pressure. To obtain a high output the maximum possible surface area of the membrane that can be achieved should be exposed to the components to be separated. 120

Operating conditions in the processes of the invention will depend mainly of the nature and method of conditioning of the membrane and also on the components to be separated. The main operating variables, however, are pressure, temperature feed rate and complex concentration. 130

In the separation of rhodium complexes from hydroformylation products temperatures up to about 60°C. and concentrations up to 2% by wt. are preferred.

5 The present invention is illustrated with reference to the flow system apparatus described in the accompanying drawings, in which;

15 Figure 1 shows schematically the high pressure flow system used.

In Figure 1 feedstock was supplied from a reservoir 1 at atmospheric pressure, to which dry nitrogen could be supplied if necessary via line 8. The feedstock was pressurised by means of a hydraulic ram pump 2 and supplied to the cell 3. Permeated material left the cell to collection via line 4. Non-permeated material returned to the reservoir 1 via a felt filter 5 and a pressure control valve 6. A cell by-pass line 7 was provided containing a pressure relief valve 9 operating at 3000 psig. Pressures were read from gauge 10.

25 In Figure 2 a 150 ml, stainless steel, nitrogen pressurised cell comprises three parts, top 2 and base 7 plates and barrel 5 held together by four rods 4. The membrane 10 having a permeable area of 11.4 cms<sup>2</sup> is supported on a sintered stainless steel disc 11 of pore size 6 microns seated in the base plate 7. The seal between the membrane 10 and the barrel 5 is made with a 1 mm rubber gasket 8 and between plates 2 and 7 and barrel 5 by O rings 3. The top plate 2 contains a relief valve 1 and a connector to the nitrogen supply. Turbulence in the cell is maintained by magnetic stirrer 6.

35 In Figure 3 a stainless steel high pressure cell is shown. A membrane 11 7.8 cms in diameter (permeable area 23 cm<sup>2</sup>) is cushioned by filter paper 18 and is supported on a sintered stainless steel disc 12 (of 6 pore size) resting in a circular recess 19 in the cell base 13. Gramophone grooves 20 cut into the bottom of the recess facilitate permeate recovery 17. Six Allen capped screws 21 secure the cell top 14 and base 13 together, thereby sealing the membrane 11 against a nitrile 'O' ring 15 carried in the cell top 14. An outer 'O' ring prevents permeate linking to the outer edge of the sintered disc 12 and returning into the feed. To create turbulence in the cell, feedstock enters through a 1 mm orifice 16. The dead volume of the cell is 3.5 mls.

The flow system and apparatus described

55 were used to investigate the separation of a rhodium complex from organic liquids, and conditions and the results obtained are given in the following Examples. In these investigations rates of permeation (PR) per unit area of membrane were determined by measuring the volume of permeate collected over known periods of time. The metal contents of the permeates and feedstocks were measured by X-ray fluorescence so that the resistance of the membrane to catalyst permeation could be expressed in terms of solute retention, where solute retention was the ratio, expressed as a percentage, of the difference between the metal content of the feedstock and the permeate to the metal content of the feedstock. Metal weight balances were made in selected cases so as to determine the quantitative nature of the separation. In these cases the metal content of the membrane itself was determined after dissolution in dioxan.

75 The invention is illustrated by the following Examples, in which the high pressure flow system shown in Figure 1 was used.

#### EXAMPLES 1-8

80 Membranes were prepared by immersing glass slides in a 1-2 per cent solution of polyethylene\* in xylene at 100 to 130°C., allowing about 1 hour for equilibration and withdrawing the slides at the rate of about 2 cms per second. The membranes were formed on the glass slides by allowing the xylene to evaporate at room temperature. The membranes were then removed by immersing the slides in cold water and floating the film from the glass. The membranes were removed from the water surface by floating onto a filter paper (Gelman Metrical Filter Type G.A.9 O.I.  $\mu$  pore size). The membranes were then dried or used directly in an ultrafiltration cell in which the membrane and filter are supported on a sintered stainless steel disc (5 $\mu$  pore size). The membranes were then used to separate a rhodium complex of formula



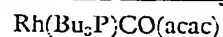
100 where acac = acetylacetonate from toluene or *n*-heptaldehyde solvents. The results are shown in Table 1.

\* The polyethylene used was "Rigidex" Type 50 as previously described.

TABLE I

Example	Thickness of Membrane (microns)	Solvent	Concn. of Complex p.p.m.	Cell	Applied Pressure psig	PR gal./ft. <sup>2</sup> /day	% Solute Retention
1	0.35	Toluene	564 — 676	Fig. 3	400 1000 2000	1.4 2.34 3.9	98 96.5 94 — 97
2	0.35	n-heptaldehyde	600 — 708	Fig. 3	1000 1500 2000	0.78 0.97 1.04	83 87 88
3	0.57	n-heptaldehyde	660 — 708	Fig. 3	500 1000	1.45 2.4	95.5 92.5
4	0.35	n-heptaldehyde	660	Fig. 3	1500	0.75	96.0
5	0.3	n-heptaldehyde	644	Fig. 3	1500	1.4	89.0
6	0.34	Toluene	704	Fig. 2	100	0.34	99
7	0.5	Toluene	704	Fig. 2	100	0.51	98
8	0.5	n-heptaldehyde	708	Fig. 2	100	0.04	90

## EXAMPLES 9—15



Polyethylene membranes prepared as previously described were used to separate a rhodium complex of formula

from the mixture obtained by the hydroformylation of propylene or hexene.

TABLE 2

Example	Thickness of membrane microns	Feed	Cell	Applied pressure psig.	Permeation rate gall/ft <sup>2</sup> /day	Solute Retention
9	0.35	C <sub>7</sub> aldehyde containing 170 ppm of Rh compound	Fig. 3	1000 1500 2000	0.79 0.97 1.04	83 87 88
10	0.57	„	Fig. 3	500 1000	1.45 2.4	92.5 95.5
11	0.35	„	Fig. 3	1500	0.75	96.4
12	0.3	„	Fig. 3	1500	1.4/4 days	89.0
13+	0.3	„	Fig. 3	1500	0.75/6 days	89.0
14	0.3	HE (92 ppm of Rh compound)	Fig. 2	500	0.01	33.0
15*	0.4	„	Fig. 2	500	0.08	

+ after drying for 24 hours at 94°C.

\* Test at 90°C.

HE = heavy ends, that is the mixture obtained from the hydroformylation of propylene, from which propylene and components boiling below 120°C have been removed.

## EXAMPLES 16 — 21

TABLE 3

Example	Composition of Membrane % by weight	Applied Pressure psig	Permeation Rate gall/day/ft <sup>2</sup>	% Retention Rh acac
16	100PP	1000 1500	12.4 13.8	>99 >99
17	100P4	500	28.1	61.7
18	100P4	1000	37.5	61.7
19	25P4 } blend 75PP }	500 1000 1500	18.4 24.5 24.1	86.8 87.5 83.8
20	5P4 } blend 95PP }	1000 1500	19.4 24.4	>99 97.3
21	5P4 } blend 95PP }	500 1000 1500	21.7 28.1 29.9	93.8 96.3 92.5

P4 = poly-4-methylpentene-1 (BP)

\* not determined

PP = polypropylene (I.C.I.) designated GW 522M

5 The poly - 4 - methylpentene - 1 used was an isotactic polymer obtained from BP Chemicals having a Limiting Viscosity Number of 4.0, a crystallinity 98% (i.e. 98% insoluble in boiling heptane) and a density of 0.833 gm/ml.

10 The membranes were prepared by casting from a 1—2% solution in hot toluene and were 0.3—0.4 $\mu$  in thickness. The membranes were used to separate Rh(Bu<sub>3</sub>P)CO(acac)

from a solution containing 100 ppm of rhodium (as the complex) in toluene. The results are shown in Table 3.

## EXAMPLES 22—24

Results of the annealing treatment are recorded for different membranes in Table 4. The membranes were prepared as previously described.

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TABLE 4

Permeation Data on Annealed and Unannealed Polyolefin Membranes

Example	Membrane	Thickness $\mu$ m	Annealing Conditions in Toluene	Pressure kN/m <sup>2</sup>	Permeation Rate l/h/m <sup>2</sup>	Solute Retention Rhacac
22	High density polyethylene +	0.35 0.35	None 2½h at 83°C	3450 3450	8 41	>97.5 >97.5
23	Polypropylene*	0.44 0.35	None 2½h at 93°C	3450 3450	20 97	>97.5 >97.5
24	Poly-4-methyl- pentene-1 (5%) + polypropylene (95%)	0.35 0.48	None 2½h at 93°C	3450 3450	36.5 118	>97.5 83

Feed — Toluene containing Rhacac (106 ppm Rh)

+ polyethylene obtained from BP Chemicals Limited Rigidex Type 50 density about .96 g/ml.

\* polypropylene obtained from I.C.I. Limited designated as general purpose type GW 522M density 0.91 gm/ml.

## WHAT WE CLAIM IS:—

1. A process for the separation of an organometallic compound from a solution of the compound in an organic component, which comprises bringing the solution into contact with one side of a polyolefin membrane at an applied pressure greater than the pressure on the opposite side of the membrane, the pressure differential being greater than the osmotic pressure of the system and the molecular cross section of the organometallic compound being greater than that of the organic component and collecting the organic components which permeate the membrane, the permeate having a reduced content of the organometallic compound.

2. A process as claimed in claim 1 wherein the separation process is effected at a temperature of from 0 to 100°C.

3. A process as claimed in either of claims 1 or 2 wherein the thickness of the membrane is in the range 0.05 to 100 microns.

4. A process as claimed in any one of claims 1 to 3 wherein the applied pressure is up to 2500 psig.

5. A process as claimed in claim 4 wherein the applied pressure is in the range 100 to 2000 psig.

6. A process as claimed in any one of claims 1 to 5 wherein the membrane, before use, has been subjected to an annealing treatment by immersing in an organic solvent for a period up to 20 hours at a temperature above 50°C. but below the dissolution temperature.

7. A process as claimed in claim 6 wherein the annealing treatment has been effected at

a temperature from 80 to 100°C. for a period of from 1 to 20 hours.

8. A process as claimed in either of claims 6 or 7 wherein the organic solvent is toluene.

9. A process as claimed in any one of claims 1 to 8 wherein the concentration of organometallic compound is up to 5% by wt.

10. A process as claimed in claim 6 wherein the concentration of organometallic compound is up to 20,000 ppm by wt.

11. A process as claimed in any one of claims 1 to 10 wherein the polyolefin membrane is polyethylene, polypropylene, poly-4-methylpentene - 1, polystyrene, or a blend thereof.

12. A process as claimed in any one of claims 1 to 10 wherein the polyolefin membrane is a copolymer of monomers selected from ethylene, propylene and 4-methylpentene - 1.

13. A process as claimed in any one of claims 1 to 12 wherein the organometallic compound is a transition metal co-ordination complex.

14. A process as claimed in claim 13 wherein the complex contains a metal of Group VIII or VIIA or VA of the Periodic Table according to Mendeleef.

15. A process as claimed in claim 14 in which the metal complex is a rhodium complex.

16. A process as claimed in claim 15 wherein the complex is  $\text{Rh}(\text{Bu}_3\text{P})\text{CO}(\text{acac})$  or  $\text{Rh}(\text{Bu}_3\text{P})_2\text{CO propionate}$  where Bu represents *n*-butyl and acac is acetylacetonate.

17. A process as claimed in claim 15 where-

in the metal complex is  $\text{Rh}(\text{Et}_3\text{P})_2\text{COCl}$ ,  $\text{Rh}(\text{iPr}_3\text{P})_2\text{COCl}$  or  $\text{Rh}(\text{Bu}_3\text{P})_2\text{COCl}$  where Et is an ethyl radical, iPr is an isopropyl radical and Bu is a *n*-butyl radical.

- 5 18. A process as claimed in claim 14 wherein the metal complex is nickel acetylacetonate or a nickel or vanadium porphyrin.

- 10 19. A process as claimed in any one of claims 1 to 18 wherein the mixture comprises alkenes having up to 20 carbon atoms per molecule.

- 15 20. A process as claimed in any one of claims 1 to 18 wherein the mixture comprises the reaction product of the hydroformylation of a lower olefin in the presence of carbon monoxide and hydrogen.

21. A process for the separation of an organometallic compound substantially as

hereinbefore described with reference to any of the Examples.

22. Organometallic compounds whenever separated by a process as claimed in any of claims 1 to 21.

23. A continuous process involving homogeneous catalysis which comprises reacting a hydrocarbon in the presence of a co-ordination complex of a transition metal in which a solution of the co-ordination complex in the liquid reaction mixture is produced and separating the co-ordination complex from the reaction mixture by a process as claimed in any of claims 1 to 21.

J. WOOLARD  
H. L. EASTMAN  
Agents for the Applicants.

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FIG.1.

